THERMAL ANALYSIS

INTRODUCTION

A set of bodies (substances) constituting the object of our analyses at a given moment is referred to as a **system**, while everything outside is called the **surroundings**. Individual uniform elements of the system separated from the others by distinct boundary surfaces are termed **phases** of this system. In the system composed of water, ice, and water vapour, we have only one substance but three phases: ice, water, and its vapour. These phases are in different states of matter, and the transition of any phase of the system from one state to another is called the **phase transition**. The phases may be homogeneous (pure water) and heterogeneous (colloidal solutions). Every system is created of a certain number of independent components, i.e., substances required to constitute all the phases of the system. For example, the *ice-water-water vapour* system is a three-phase, but one-component system. The *chloroform-acetic acid-water* system is a three-component, one-phase system.

The number of phases P in every system depends on factors (parameters) such as pressure p, temperature T, and composition (expressed in concentrations c), *etc*. The number of parameters, which can be changed with no change in the number of phases - either by elimination or the formation of a new phase, is called the number of **degrees of freedom** of a system. The **phase rule** proposed by Gibbs describes the relationship between the number of degrees of freedom F, the number of phases P, and the number of components C in each system. The rule specifies that the sum of the number of phases and the degrees of freedom in any system equals the number of components increased by two. This dependence can be expressed by the equation:

$$P + F = C + 2 \tag{1}$$

Systems composed only of solid and liquid phases while lacking the gaseous phase are called **condensed systems**. They are found where the external pressure exceeds the pressure of saturated vapour at a given temperature. These include, e.g., metallic and silicate systems of certain organic compounds.

Stabilization of pressure in these systems results in a reduction of the number of degrees of freedom by one. Hence, the phase rule takes the form:

$$P + F = C + 1 \tag{2}$$

In a condensed binary (two-component) system under isobaric conditions (constant pressure), the system has one degree of freedom when two phases (e.g., a liquid solution and a solid phase) are found in equilibrium. It means that under these conditions, one parameter is sufficient to unambiguously determine the state of this system. It may be the temperature or concentration of one of the components in one of the phases. In other words, the temperature at which two phases in the condensed binary system may coexist in the state of equilibrium under isobaric conditions determines unambiguously the concentration of the components in both phases or vice versa, the concentration of one of the components in one of the phases determines the temperature, at which both phases may coexist in the state of equilibrium. The function of the dependence between these parameters (i.e., between the temperature of coexistence of two phases and concentrations of components in these phases) presented on a graph forms the so-called **phase equilibrium diagram** for a two-component system.

If in a two-component condensed system, there are three phases, then the number of degrees of freedom equals zero. In the case when two solids and a liquid solution are the phases, then the respective point on the phase equilibrium diagram is referred to as the **eutectic point**. A system found at the eutectic point has zero degrees of freedom. Thus, the solidification of the solution at the eutectic point has to occur with no change in the composition.

A mixture of fine crystals of components A and B, which is separated under such conditions, is called a **eutectic mixture**, while the temperature at which solidification takes place in the entire solution of the eutectic composition is referred to as the **eutectic temperature**. The **thermal analysis** consists of the determination of the so-called cooling curves (temperature = f(time)) for pure components of the investigated system and the series of their mixtures and based on that - the preparation of a phase equilibrium diagram.

Two-component mixtures (e.g., formed from pure chemical compounds or alloys produced from pure metals) are characterised by differently shaped cooling curves than those of pure components (Fig. 1).
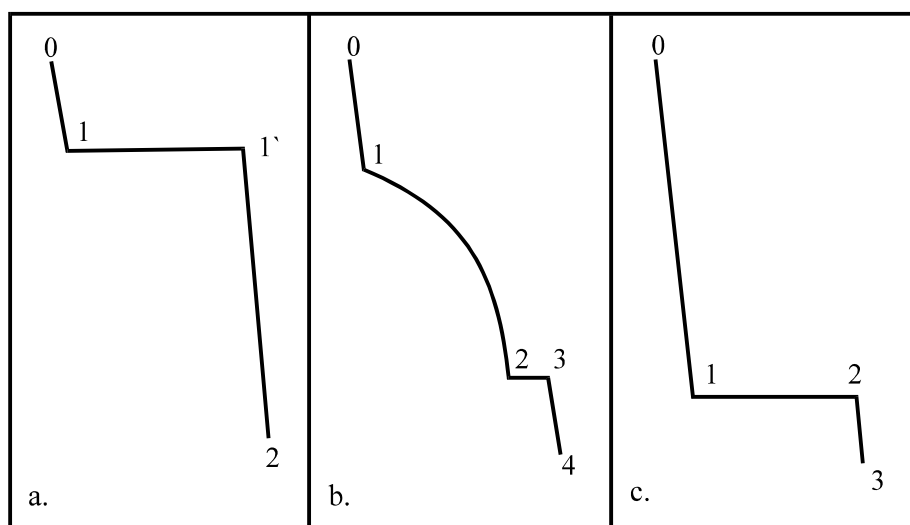
Fig. 1 a. pure substance, b. mixture, c. eutectic mixture.

During the cooling process of a pure substance, the temperature remains constant (Fig. 1a). As a consequence, a horizontal segment 1-1' on the cooling curve corresponds to crystallisation. The decrease in temperature slows down because the heat released during crystallisation compensates for heat loss caused by the release of heat to the environment as a result of the difference in temperatures. When the process of phase transition is completed (point 1'), the temperature of the sample decreases along segment 1'-2. In the case of cooling of the mixture (Fig. 1b), initially the curve runs analogously to the curve corresponding to curve 1a (segment 0-1). This range corresponds to the cooling of a two-component, one-phase liquid. Crystals of the component found in excess of the eutectic mixture composition start to separate at a temperature corresponding to point 1 (the kink of the curve). The temperature for the onset of separation of this component is lower than the temperature of the solidification of a pure substance. As a result of crystallisation of one of the components, the concentration of the other component in the solution increases constantly, thus, the solidification temperature decreases continuously along segment 1-2. Point 2 corresponds to the system reaching the eutectic composition and the solidification temperature of the eutectic mixture. At the eutectic point, three phases coexist (two solid and one liquid), thus, during the solidification process s = 0. This explains the constancy of temperature during the solidification process, which is manifested in the horizontal direction of segment 2-3. Segment 3-4 corresponds to the cooling of a system composed of two solid phases. The eutectic mixture is characterised by a similar curve (Fig. 1c) to that for a pure component, except for the fact, that the segment corresponding to the solidification temperature is located much lower.

The phase equilibrium diagram (Fig. 2) is prepared by dividing the X-axis into 100 parts for plotting the percentage composition of specific alloys or mixtures. The Y-axis is used to plot temperatures of phase

transitions for pure components A and B as well as starting and final temperatures of solidification for individual tested mixtures 1, 2, 3, and 4.
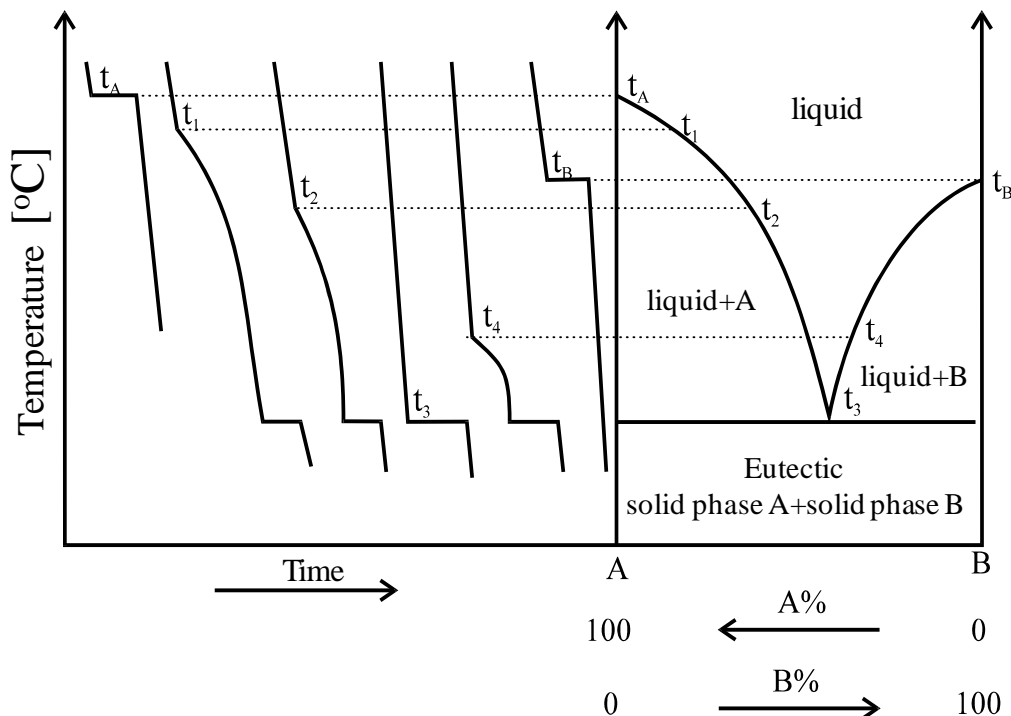

Fig. 2 The structure of the phase equilibrium diagram based on cooling curves

On the thus prepared phase equilibrium diagram (Fig. 2), phases found within a given field of the graph are marked. Phase equilibrium diagrams make it possible to determine concentrations of phase components found in an alloy or mixture at a specific temperature and for a known composition, and to determine the ratio of phases under such conditions.

More examples of phase diagrams are to be found here:
http://www.doitpoms.ac.uk/miclib/phase_diagrams.php

OBJECTIVE OF THE TASK

- to determine the eutectic point (eutectic composition and temperature).

APPARATUS AND GLASSWARE

- a sand bath
- an electronic thermometer – a METEX universal multimeter with a temperature sensor (thermocouple)
- porcelain crucibles – 6 pieces
- a spoon
- crucible tongs

CHEMICALS

- phthalic anhydride
- naphthalene

EXPERIMENT PROCEDURES

1. Prepare 6 samples of naphthalene-phthalic anhydride mixture according to the following compositions:

Sample no.	1	2	3	4	5	6
Naphthalene	-	1.5g	2.5g	3.5g	4.25g	5g
Phthalic anhydride	5g	3.5g	2.5g	1.5g	0.75g	-
total	5g	5g	5g	5g	5g	5g

2. Start the computer.
3. Start the METEX SCOPEVIEW program from the icon on the screen and the METEX meter.
4. In the METEX SCOPEVIEW program
   - click POWER to verify communication with the meter (the program should start recording readings of the meter)
   - next click SCOPE to activate the panel controlling the system
   - set a specific range of temperatures (from 40 to 200°C - as specified by the instructor) and sampling at 20 s intervals
   - name the file before the measurement (by pressing RECORD)
   - click SCOPE to activate the recording panel
   - measurement recording is initiated after clicking RUN and upon completion, it is stopped by clicking STOP
   - **Follow the manual instructions presented for the task and information given by the instructor**.
5. Heat sample 1 to the temperature of approx. 150°C in a sand bath, then remove the sample from the bath, place it under the stand, and immerse the temperature probe in the mixture.
6. Initiate measurement recording by clicking RUN.
7. When sample temperature drops to 40°C complete measurements by clicking STOP.
8. Repeat measurements for successive samples.

Heat each mixture to a temperature of approx. 150°C (heat sample 6 only to approx. 90°C).

Caution!
After the mixture solidifies again transfer the crucible to the bath and remove the probe only after the sample melts; **pour the crucible contents into a specially labelled container**.
Do not pour the crucible contents into the sink!!!

PREPARATION OF RESULTS

1. Calculate the percentage composition of mixtures.
2. Plot cooling curves for all samples (temperature - time).
3. Based on the course of the cooling curves determine the temperatures of kinks and stops.
4. Prepare the phase equilibrium diagram of the tested system.
5. Determine the composition and temperature of the eutectic mixture.

Template of the table and draft of the study

………………………….. *Faculty* ………………………….. *Field of study* *Full-time/ part-time studies*	………………………………………… *Name and surname*	………………………………….... *Date:*
Group no.: ………………… Team no.: …………………	………..…………… *Exercise no.:*	………………………………….. *Instructor:*

………………………….. *Wydział* ………………………….. *Kierunek* *Studia stacjonarne/niestacjonarne*	………………………………………… *Imię i Nazwisko studenta*	…………………………………... *Data wykonywania ćwiczenia:*
Nr grupy: ………………….. Nr zespołu: ………………..	………..…………… *Nr ćwiczenia:*	………………………………….. *Nazwisko Prowadzącego:*

1. Temat ćwiczenia
2. Cel ćwiczenia:
3. Wstęp teoretyczny:
4. Pomiary:
5. Obliczenia:
6. Wykresy:
7. Wnioski

1. Exercise title:
2. The aim of the exercise:
3. Theoretical introduction:
4. Results:
5. Calculations:
6. Graphs:
7. Conclusions: